Some Transformations
of
Parasulphaminebenzoic Acid

(Under Influence of Heat and by Action of
Phosphorus Pentoxide or Pentachloride.)

Dissertation

Submitted to the Board of University Studies
of the Johns Hopkins University for the degree
of Doctor of Philosophy,

by

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Acknowledgement

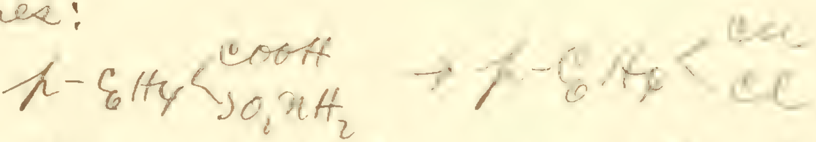
This investigation was carried on under the guidance of Prof. Ira Remsen, for whose kind encouragement and helpful instruction throughout my sojourn at this University I desire to express my grateful appreciation. I am glad also to acknowledge valuable instruction at the hands of Prof. H. N. Morse.

Introduction

In 1889 Remsen and Dohme[1] showed that by the action of phosphorus pentachloride on benzoic sulphinide, orthochlorbenzoic nitrile is formed:

$$o\text{-}C_6H_4\left<{CO \atop SO_2}\right>NH \rightarrow o\text{-}C_6H_4\left<{CN \atop Cl}\right.$$

In their article mention is made of the fact that the same reaction took place by similar treatment of the corresponding compound of the para series:



$$p\text{-}C_6H_4\left<{COOH \atop SO_2NH_2}\right. \rightarrow p\text{-}C_6H_4\left<{CN \atop Cl}\right.$$

The nitrogen of the benzoic sulphinide is combined with both the carbon and the sulphur, and derivatives of it would not be unlooked-for, in which the nitrogen is combined wholly with the carbon or the sulphur. But the nitrogen of parasulphaminebenzoic acid is conceded to be combined with sulphur and not with carbon, and the two substituting groups are in all pro-

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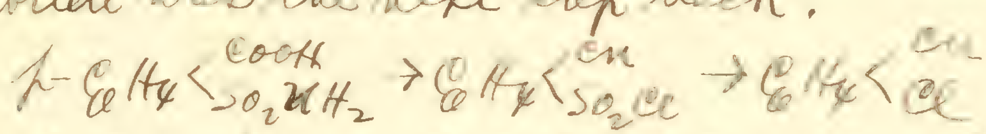
[1] Am. Ch. Jour. 11-347.

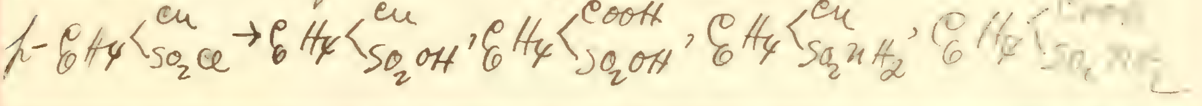
bability farther apart in space. The shifting of the nitrogen atom under such circumstances, therefore, made the latter reaction a very remarkable one.

With the object of finding, if possible, any intermediate products of the change from parasulphaminebenzoic acid to parachlorbenzoic nitrile, Hartman[1], working in this laboratory, made a more thorough study of the subject, showing conclusively that paracyanobenzenesulphone chloride was the next step back:



$$p\text{-}C_6H_4<^{COOH}_{SO_2NH_2} \rightarrow C_6H_4<^{CN}_{SO_2Cl} \rightarrow C_6H_4<^{CN}_{Cl}$$

Hartman showed that this intermediate product gave off sulphur dioxide, when heated, and passed over to the end-product. By either substituting the chlorine or saponifying the nitrile of the former, or combining both of these, he fully established the constitution of the new product:



$$p\text{-}C_6H_4<^{CN}_{SO_2Cl} \rightarrow C_6H_4<^{CN}_{SO_2OH},\ C_6H_4<^{COOH}_{SO_2OH},\ C_6H_4<^{CN}_{SO_2NH_2},\ C_6H_4<^{COOH}_{SO_2NH_2}$$

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[1] Dissertation, Johns Hopkins University, 1894.

There could therefore be no doubt about the transformation by which nitrogen shifts from a position connected with sulphur to one connected with carbon. But the important question as to how this fundamental change takes place, was still open. In the short time available at the close of the academic year, Hartman[1] studied the effect of heating parasulphaminebenzoic acid alone, in order to learn whether in this case there is any shifting of nitrogen. His results will be taken up later.[2]

I. Influence of Heat on Parasulphamine-benzoic Acid

Preliminary Experiments

Hartman's results as obtained by heating the acid, were first studied more fully, with a view to their verification. He stated that the acid, when heated to its melting-point, 285°, or for a long time at 235°, becomes soluble without

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[1] Dissertation, page 28

[2] See below.

loss in weight. This last statement was fully verified by a series of experiments, which are tabulated below:

No	Weight in grams of acid heated	Weight in grams of acid after heating	Temperature of heating	Length of heating in hours
I.	10.962	10.9655	220°	8
II.	4.56	4.525	225°	6
III.	4.8395	4.8475	235°	3
IV	4.0235	4.026	235°	4
V.	3.9339	3.922	285°	3
VI.	5.9001	5.886	285°	8

It is evident that there is no loss in weight other than the slight variation due to experimental error. The resulting mass, if it had been heated to 285°, was indeed found to be completely soluble in water, but if heated at 220°-235°, there was always formed an insoluble product. Hartman further states that acid ammonium-parasulphobenzoate is formed as a result of the heating.

This observation was corroborated, as will be shown later.[1]

Outline of Fundamental Process

A cylindrical air-bath is surrounded with asbestos so that by use of one Bunsen burner the temperature within may be raised as high as 300°. The bath is covered with a glass plate, in the center of which a half-inch hole is made for the insertion of thermometer and cork. The temperature is regulated by means of a screw-clamp on the tubing of the burner. The parasulphaminebenzoic acid to be heated is ground very finely and placed in a small evaporating dish. The dish is covered with a watch-glass, in the center of which is a small hole for the insertion of the thermometer. The bath is first regulated to the desired temperature, then the dish is lowered to the shelf half-way down; the whole is covered with the glass-plate and the thermometer is inserted to

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[1] This dissertation, page 42.

the bottom of the dish. By this means, evenness of temperature and accuracy of observation are obtained, while the observer can see the substance and note the temperatures at which changes set in.

The Heating at 285°

A qualitative study showed that the mass resulting from heating para-sulphaminbenzoic acid for three hours at its melting-point, 285°, was insoluble in benzene, ether, and ligroïn, but wholly soluble in alcohol or water. Longer heating was not found advisable. The opaque water solution was purified as much as possible by boiling with animal charcoal, and when filtered, evaporated to crystallization. The crystals, which completely filled the liquid, had every appearance of acid ammonium parasulphobenzoate. By adding barium chloride to this solution, the corresponding barium salt appeared, which on crystallization assumed its characteristic form, as described by Remsen[1]. The crystals

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[1] Annalen 178-290.

were identified[1] by comparison with known specimens of acid ammonium parasulphobenzoate.

The mother liquor from these crystals was evaporated to crystallization with a little barium chloride. There then appeared seed-like crystals throughout the liquid. These were recrystallized, when they appeared in the same form. This substance was slightly acid and gave off ammonia on boiling with alkali. Analysis showed that it had the same composition as acid barium parasulphobenzoate, but no needles could be obtained from it. It was obtained in very small quantity, and may contain a new acid:

0.3845 grams barium salt lost 0.035 grams H_2O and gave 0.1493 grams $BaSO_4$

	Calculated for $(C_6H_4\langle^{COOH}_{SO_2O})_2Ba.3H_2O$	Found
H_2O	9.11	9.10
Ba	23.10	22.83

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[1] This dissertation, page 42.

In one experiment there was obtained a small quantity of a neutral barium salt that was insoluble in all solvents tried. When put into concentrated sulphuric acid, it turned red and decomposed. It is probably a product of the charring.

But the main result is the formation of acid ammonium parasulphobenzoate:

$$p\text{-}C_6H_4\left\{\begin{matrix}COOH\\SO_2NH_2\end{matrix}\right. + H_2O(\text{from charring}) = C_6H_4\left\langle\begin{matrix}COOH\\SO_2ONH_4\end{matrix}\right.$$

Very little free acid is formed above that required for this main product, a fact indicated by two experiments. (1) Following the analogy of the other heatings[1] the whole water solution was in one case evaporated to successive crystallizations until the residue was very small. It was found that this latter contained a proportionately large amount of ammonia. (2) Solutions of alcoholic potash and sulphuric acid were standardized against potassium tetroxalate and parasulphaminebenzoic acid. Then a weighed quantity of the latter was heated to 285°

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[1] This dissertation, pages 41 and 44.

and after cooling was dissolved in water. The acidity of the solution was now determined by titration of the potash, litmus paper being the indicator. After this, excess of alkali was added and the ammonia distilled into standard acid. I. required 25 cc. of 0.823 normal alkali for neutralization and contained ammonia sufficient to neutralize 22.7 cc. of acid. II. required 17 cc. standard alkali and 17.7 cc. standard acid. The acidity was calculated in grams of parasulphobenzoic acid. The total weight of this was, of course, obtained by adding the weight as calculated from found acidity to the weight that the found ammonia had neutralized. This, plus the ammonia, gave the total matter found by titration.

No.	Weight in grams of substance heated to 275°	Length, in hours, of heating.	Weight in grams of free acid found	Weight in grams of ammonia found	Weight in grams of acid in form $C_6H_4\genfrac{}{}{0pt}{}{COOH}{SO_2ONH_4}$	Total Matter found by Titration
I.	5.4001	8	2.078	0.32	0.181	4.501
II.	3.4331	3	1.579	0.248	0.108	3.297

Thus, on an average, only about four per cent

of the acid present is in excess of that required for acid ammonium parasulphobenzoate. This is not true of lower heatings[1]. The charring appears to increase with length of heating, as shown by comparison of the third column with the last.

Comparison of the Heatings between 220° and 235°

By use of the air bath described[2], 220° was noted to be the lowest temperature at which parasulphaminebenzoic acid would fuse. The acid was heated at 190° for two hours, at 195° for one hour, at 200° for one hour and so on, until 220° was reached, when it began to fuse and darken. If heated at temperatures much above 235°, the charring was too great for even approximate neatness of reaction. When heated within this range of temperature, a substance always resulted that was insoluble in water, and several experiments were made to ascertain the percentage of this formed;

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[1] This dissertation, page 11. [2] This dissertation, page 5.

No.	Weight in grams of substance heated	Weight in grams of insoluble material	Percentage found of insoluble material	Temperature of heating	Length of heating in hours
I	10.962	2.512	22.91	220°	8
II	5.557	1.1338	20.4	223°	8
III	4.06	0.7645	18.93	225°	6
IV.	6.132	1.1601	18.93	225°	6
V.	4.023	0.4825	11.98	235°	8

Evidently, 220° is the best temperature for the formation of the insoluble substance. In the above heatings, not a trace of sulphaminic acid remained undecomposed.

Two quantitative determinations were made at 223° and 225° by the same method as for 235°.[1] I. 5.557 grams parasulphaminebenzoic acid, heated to 225°, treated with water and filtered,[2] gave 1.1338 grams of insoluble product, and required 33.2 cc. of 0.823 normal potash to neutralize the filtrate, from which sufficient ammonia was distilled to neutralize 14.8 cc. standard acid. II. 6.1324 grams, heated to 223°,

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[1] This dissertation, page 8. [2] This dissertation, page 15.

gave 1.1007 grams of insoluble product, 25.6 cc. of standard potash and 22.1 cc. of standard acid.

No.	Percent of insoluble product	Percent of free acid in filtrate	Percent of free acid calculated	Weight in grams of [illegible] found	Weight [illegible] calculated
I.	20.4	47.64	50.24	0.202	0.276
II.	18.93	49.61	"	0.309	0.320

Although the percentage of insoluble product varies with temperature, the percentage of acidity is apparently a constant and agrees practically with the theory; for 50.24 grams of parasulphobenzoic acid will neutralize as much base as 100 grams of parasulphaminebenzoic acid. Stated in other words, the filtrate from the mass heated at 220°-235°, will neutralize as much standard alkali as it would have neutralized before it was heated. This is not at all true of higher temperatures tried.[1]

The Diamides of Parasulphobenzoic Acid

A. The Infusible Diamide

Examination showed that the insoluble product

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[1] This dissertation, page 9.

formed in the manner already indicated,[1] is neutral toward litmus, unaffected by carbonates, soluble slightly in boiling water, insoluble in cold and hot alcohol, and infusible. It gives off ammonia copiously on boiling with alkali, but in general has properties akin to those of an ordinary amide.

<u>1. Analysis</u>. – The results lead to the formula, $C_7H_8O_3N_2S$, which corresponds with that of para-sulphobenzoic diamide, $p\text{-}C_6H_4\Big\langle{CO.NH_2 \atop SO_2.NH_2}$:

I. 0.2118 gram gave 0.3264 gram CO_2 and 0.01 gram H_2O.

II. 0.1855 gram gave 0.286 gram CO_2 and 0.0709 gram H_2O.

III. 0.2455 gram gave 29.5 cc. of nitrogen at 18.4° and 762 mm.

IV. 0.2102 gram gave 25.76 cc. of nitrogen at 19.8° and 762 mm.

V. 0.1761 gram gave 0.2038 gram $BaSO_4$, Carius method.

	Calculated for $C_6H_4\Big\langle{CONH_2 \atop SO_2NH_2}$	I.	II.	III.	IV.	V.
C	42	42.02	42.04			
H	4	4.51	4.25			
N	14			14	14.14	
S	16					15.9

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[1] This dissertation page 10.

2. Process of Purification.—Whether the heated mass is extracted with alcohol or water, the residue is the same. But alcohol extracts more slowly, especially the last traces of isoparasulphaminebenzoic acid.[1]

Heat parasulphaminebenzoic acid at 221° for eight hours, then, after cooling, powder the mass thus obtained. Treat with cold water, boil, and set aside the liquid over night, after which the whole is placed on a filter. The diimide is washed thoroughly with cold water, then dissolved in caustic soda solution, treated with about double its weight of purified animal charcoal, stirred intermittently for an hour, and filtered as rapidly as possible by use of a suction-pump. As soon as filtered, the solution is treated with a slight excess of hydrochloric acid, when the substance appears in its characteristic crystalline form. It must then be washed with water until the washings contain no chlorine.

It appears that the infusible diimide, when

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[1] This dissertation, page 48.

first formed, is in a very finely divided condition; for, if filtration is attempted at once, after treating the powdered mass with water, some of the diamide will always pass through the filter. The decanted filtrate will after a few days deposit small, glistening plates, identified as the infusible diamide. If, however, the mass is boiled with water, and let stand about twelve hours, the filtration is easy and the filtrate will not deposit crystals on standing. In purifying the substance with animal charcoal, care must be taken to use enough thereof, to keep the liquid cold, and to filter and acidify as soon as possible; for, as will be shown later[1], the infusible diamide is decomposed by alkaline hydroxide in amounts increasing with time and temperature. As an extra precaution, it is well finally to triturate the diamide with sodium carbonate solution, and afterwards wash well with water.

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[1] This dissertation, page 21.

3. Properties.—The infusible diamide may be crystallized from boiling water, but it is so difficultly soluble that this method is not advisable, especially since it appears in crystalline form, easily washed, when precipitated from alkaline solution. The compound is characterized by its marked insolubility. Neither benzene, ligroïn, chloroform, ether, nor alcohol dissolves it. It is just as stable towards acids as it is unstable towards alkalis. Sodium hydroxide solution decomposes it even at temperatures below 0°, while boiling hydrochloric acid and nitric acid do not affect it. It dissolves readily even in cold concentrated sulphuric acid, and this solution may be heated to 200° without decomposition, since on cooling and pouring into water, the characteristic crystals again appear. The crystals consist of small plates, minute when precipitated, and best formed by crystallization from water. If excess of acid is added to its diluted alkaline solution, the

minute plates appear slowly and occasionally arrange themselves abreast, forming apparent needles, that upon the slightest agitation break up into their true form. Even phosphorus pentachloride apparently does not affect it; for when heated with this reagent at 200° for several hours, the diamide was regained unchanged. It is practically insoluble in comparatively concentrated sodium hydroxide solution.

4. Saponification with HCl.— A quantity of the infusible diamide was heated with hydrochloric acid in a sealed tube to 200° for six hours. After evaporation of the acid, there was a very small quantity of some substance undissolved in the water added. Several separate heatings of pure specimens each gave this insoluble product, but in too minute quantities for other than a qualitative study. It was of acid character, insoluble apparently in hot and cold water, very soluble in alcohol, and was fu

cipitated by acids from alkaline solution in silky form. It volatilized without melting.

But most of the product is soluble in water. This solution was evaporated to crystallization, when long and interwoven prisms like acid ammonium parasulphobenzoate[1] were obtained. These were dissolved in water, and barium chloride added, when the corresponding acid barium salt was precipitated in silky form. After one crystallization from hot water, this salt appeared in its characteristic, long needles, which on analysis gave the following results:

0.2455 gram lost 0.0221 gram H_2O at 200° and gave 0.0957 gram $BaSO_4$

	Calculated for $\left(C_6H_4{<}\begin{smallmatrix}COOH\\SO_2O\end{smallmatrix}\right)_2Ba\cdot3H_2O$	Found
H_2O	9.11	9.00
Ba	23.10	22.92

The mother-liquor from the acid ammonium salt crystals was evaporated farther, when there appeared as a residue crystals of the form and properties

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[1] This dissertation, page 42.

of ammonium chloride. This saponification may therefore be expressed by the following equation:

$$p\text{-}C_6H_4\left\langle{}^{CONH_2}_{SO_2NH_2}\right. + HCl + 2H_2O = C_6H_4\left\langle{}^{COOH}_{SO_2ONH_4}\right. + NH_4Cl$$

5. Saponification with Alkali. – A quantitative experiment was made to ascertain what proportion of total nitrogen came off in form of ammonia. 1.0555 grams of the infusible diamide was placed in a small flask, about 20 cc. of dilute sodium hydroxide was added, and the ammonia distilled into an excess of 0.823 normal sulphuric acid. Titration showed that 12.75 cc. had been neutralized by the ammonia.

	Theoretically possible	Found
Percent NH_3	17.0	16.8

The contents of the flask were then examined. After neutralization with hydrochloric acid and evaporation to dryness, the mass was extracted with methyl alcohol, and the dried extract come forward to crystallization with barium chloride. There were thus obtained crystals of the appearance of neutral barium parasulphobenzoate,[1] which were recrystallized and

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[1] Annalen, 178-[illegible]

analyzed as follows:

0.7745 gram lost 0.0751 gram H_2O at 150° and gave 0.484 gram $BaSO_4$.

	Calculated for $(C_6H_4<\substack{COO\\SO_2O}>Ba.3H_2O$	Found
H_2O	9.65	9.63
Ba	36.73	36.50

From this neutral salt, which appears to be dissolved with more difficulty than heretofore supposed, the acid barium salt was prepared in characteristic form and analyzed:

0.5113 gram lost 0.0466 gram H_2O at 200° and gave 0.2001 gram $BaSO_4$.

	Calculated for $(C_6H_4<\substack{COOH\\SO_2O})_2Ba.3H_2O$	Found
H_2O	9.11	9.11
Ba	23.10	23.01

The action of dilute caustic soda on the infusible diamide is therefore thus expressed:

$$p\text{-}C_6H_4<\substack{CONH_2\\SO_2NH_2} + 2NaOH = C_6H_4<\substack{COONa\\SO_2ONa} + 2NH_3$$

Experiments were conducted to see whether at-

were possible to drive off only half of the ammonia, but in vain. A portion of the infusible diamide had been allowed to stand two months over strong hydrochloric acid and another dissolved in sulphuric acid, but no change had been effected. A weighed quantity was then boiled with a solution containing only half enough potassium hydroxide to drive off the total ammonia, but it was found that part of the diamide had gone over to potassium parasulphobenzoate, while part remained unchanged, no other product being detected.

No half-way product could be obtained by simply letting the infusible diamide stand in sodium hydroxide solution. Even at winter temperatures, below 0°, only a short time was required to change the nitrogen in the substance completely to the form of ammonia. Acid ammonium parasulphobenzoate was obtained by adding excess of hydrochloric acid to the fully decomposed alkaline solution. The

barium salts analyzed were made from this by precipitation and recrystallization.

I. 0.318 gram of acid barium parasulphobenzoate, obtained from letting the infusible diamide stand two weeks with sodium hydroxide at about 0°, lost 0.033 gram H_2O at 200° and gave 0.1473 gram $BaSO_4$

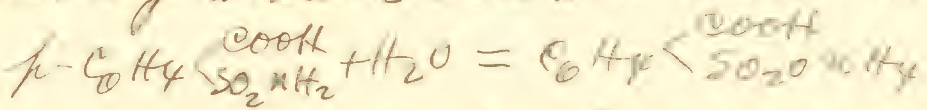
II. 0.2387 gram acid salt, obtained by similar process from reaction at about 18°, lost 0.0223 gram H_2O at 200° and gave 0.0926 gram $BaSO_4$.

	Calculated for $\left(C_6H_4<\begin{matrix}COOH\\SO_3\end{matrix}\right)_2Ba\ 3H_2O$	I. Found	II. Found
H_2O	9.11	8.93	9.34
Ba	23.10	22.92	23.34

B. The Fusible Diamide

1. Preparation. – On the supposition, at first, that the compound just considered was the ordinary diamide of parasulphobenzoic acid, $C_6H_4<\begin{matrix}CO.NH_2\\SO_2.NH_2\end{matrix}$ the idea was formed of preparing it from its mother acid, since the literature did not mention

a description of it. The following process was carried through with confident expectation of obtaining a compound identical in properties with the diamide, obtained by heating parasulphaminebenzoic acid: Acid ammonium parasulphobenzoate is first prepared,[1] best by heating the sulphamine acid to 200° with hydrochloric acid in a sealed tube:



$$p\text{-}C_6H_4{<}^{COOH}_{SO_2NH_2} + H_2O = C_6H_4p{<}^{COOH}_{SO_2ONH_4}$$

The dried product is dissolved, neutralized with a certain volume of potassium hydroxide solution, an equal quantity of the same solution added, and the ammonia distilled off. The neutral potassium salt thus obtained is evaporated to dryness and dried at 130°. It is then powdered and triturated with double the molecular quantity of phosphorus pentachloride. Reaction ensues at once, often without fusion of the mass. A goodly amount of cold water is added, and the insoluble dichloride (which may be crystallized from benzene in stout, transparent, plates) is filtered,

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[1] This dissertation, page 43.

washed well with water, and allowed to stand over night with concentrated ammonia. After the excess of ammonia is boiled off, the whole is slightly acidified, and when cold is filtered:

$$p\text{-}C_6H_4\Big<\begin{matrix}COOK\\SO_2OK\end{matrix} + 2PCl_5 = C_6H_4\Big<\begin{matrix}CO.Cl\\SO_2.Cl\end{matrix} + 2KCl + 2POCl_3$$

$$C_6H_4\Big<\begin{matrix}CO.Cl\\SO_2.Cl\end{matrix} + 4NH_3 = C_6H_4\Big<\begin{matrix}CO.NH_2\\SO_2.NH_2\end{matrix} + 2NH_4Cl$$

The product thus prepared was indeed a neutral substance, being unaffected by carbonates, and gave off ammonia on boiling with alkalis, but examination showed that it was quite soluble in hot water, from which on cooling it crystallized in needles; further, that it was soluble in alcohol and melted at 235°. These facts are sufficient to show that it is quite a different substance from the infusible diamide.

<u>2. Analysis.</u> — I. 0.2064 gram gave 0.0815 gram H_2O and 0.318 gram CO_2.

II. 0.3327 gram gave 0.1226 gram H_2O and 0.5132 gram CO_2.

III. 0.1840 gram gave 22.4 cc. of nitrogen at 20° and 773 mm.

IV. 0.1361 gram gave 16.75 cc. of nitrogen at 20° and 773.65 mm.

V. 0.1701 gram gave 0.1782 gram $BaSO_4$ (Carius)

	Calculated for $C_6H_4<^{CO.NH_2}_{SO_2.NH_2}$	I.	II.	III.	IV.	V.
C	42	42.01	42.09			
H	4	4.39	4.10			
N	14			14.10	14.12	
S	16					16.01

3. Properties – The crystals of the fusible diamide generally arrange themselves in pointed leaflets, similar in appearance to those of benzoic sulphinide. If the crystallization is allowed to proceed very slowly, the leaflike forms sometimes reach a length of one inch, each being gracefully curved, but fragile, on account of consisting of smaller leaflets. Occasionally the substance was obtained in long, curling needles from dilute solution. One striking difference between the two diamides is the fact that the infusible is precipitated in glancing plates, and the fusible in dull, milky form, by acids from alkaline solution. The latter is insoluble in benzene, ligroin, and ether, but quite soluble in hot alcohol, soluble in cold. It is

best purified by recrystallization from hot water, being difficultly soluble in the cold. Like its isomer, it is soluble in sodium hydroxide solution, unless too concentrated.

4. Saponification with Acid.— A quantity of the substance was heated with hydrochloric acid in a sealed tube to 200° for about six hours. When the tube was opened, the contents were found to be completely soluble in water. After evaporation of the hydrochloric acid, the water solution of the residue was crystallized. Well-formed crystals of acid ammonium parasulpho-benzoate filled the liquid. The acid barium salt was made from these in long, slender needles. Analysis of these showed:

0.5298 gram lost 0.0483 gram H_2O at 200° and gave 0.2073 gram $BaSO_4$.

	Calculated for $\left(C_6H_4 < {COOH \atop SO_2O}\right)_2 Ba.3H_2O$	Found
H_2O	9.11	9.11
Ba	23.10	23.00

The mother-liquor from the acid ammonium salt crystals was evaporated to dryness, and as a residue crystals of ammonium chloride were obtained. Thus, in this case, the fusible diamide is saponified like its isomer;

$$p-C_6H_4\begin{matrix}\diagup CO.NH_2\\ \diagdown SO_2.NH_2\end{matrix}+HCl+H_2O=C_6H_4\begin{matrix}\diagup COOH\\ \diagdown SO_2.NH_4\end{matrix}+NH_4Cl$$

5. <u>Saponification with Alkali</u>. – A number of trials showed without exception that, after boiling off all from the fusible diamide that will come off by use of sodium hydroxide solution, a voluminous precipitate appeared on acidifying with hydrochloric acid. Acetic acid will only accomplish this after some time, and this fact at first led to some confusion. The precipitate was fully soluble in sodium carbonate, insoluble in cold, difficultly soluble in hot water, and crystallized therefrom in short, stout needles that fused at about 280°. The barium salt was soluble, crystallizing in spherical clusters of needles, as described by Remsen[1] and by Noyes[2] for barium parasulphamine-

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[1] Annalen, 178-302. [2] Am. Ch. Jour. 7-147.

benzoate. 0.2145 gram of the salt lost 0.0313 gram H_2O at 160° and gave 0.0787 gram $BaSO_4$.

	Calculated for $(C_6H_4<^{COOH}_{SO_2NH_2})_2Ba.5H_2O$	Found
H_2O	14.35	14.59
Ba	21.85	21.64

It was found, further, that even in the cold, sodium hydroxide effected this decomposition, though much more slowly than in the case of the infusible diamide. At 18° two weeks were sufficient, but at 0°, one month was not long enough, two months being necessary. The precipitate obtained on acidifying and filtering, dissolved in both cases, completely in sodium carbonate, & melted at 280°. I. Product at 0°. 0.0735 gram barium salt lost 0.0108 gram H_2O at 160° and gave 0.0266 gram $BaSO_4$. II. Product at 18°. 0.106 gram barium salt 0.015 gram H_2O at 160° and gave 0.039 gram $BaSO_4$

	Calculated for $(C_6H_4<^{COO}_{SO_2NH_2})_2Ba.5H_2O$	I.	II.
H_2O	14.35	14.68	14.5
Ba	21.85	21.31	21.64

There can be no doubt therefore that parasulphaminebenzoic acid is the main product of the action of sodium hydroxide on the fusible diamide:

$$p\text{-}C_6H_4\left\langle\begin{matrix}CO.NH_2\\ SO_2.NH_2\end{matrix}\right. + NaOH = C_6H_4\left\langle\begin{matrix}CO.ONa\\ SO_2.NH_2\end{matrix}\right. + NH_3$$

It was accidentally discovered that barium parasulphaminebenzoate, containing five molecules of water, gradually gives this up even to the air, until it becomes practically anhydrous. Noyes[1] has shown that it does this over concentrated sulphuric acid. In the course of the present work, a very pure specimen of barium parasulphaminebenzoate had been crystallized in the cold, in form like the above, containing five molecules, and had been left standing in the air wrapped up in filter paper, for about three months. At the end of this time it was analyzed and found to be anhydrous:

0.3934 gram lost 0.0008 gram H_2O at 200° and gave 0.1702 gram $BaSO_4$.

	Calculated for $\left(C_6H_4\left\langle\begin{matrix}COO\\ SO_2.NH_2\end{matrix}\right.\right)_2Ba$	Found
Ba	25.57	25.49

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[1] Am. Ch. Jour. 7–148.

The percentage of ammonia given off by boiling the fusible diamide with sodium hydroxide solution was determined as in the case of its isomer[1]. Concordant results were not obtained, probably on account of unknown secondary decompositions, but it seems that there is given off in form of ammonia about 14 per cent of the total nitrogen above that required for quantitative decomposition into parasulphaminebenzoic acid. Experiments were conducted to see whether any parasulphobenzoic acid was formed by this decomposition. After boiling off as much ammonia as possible from the sodium hydroxide solution of the fusible diamide, hydrochloric acid was added in excess, the filtrate from the cooled product evaporated to dryness and extracted with methyl alcohol[2]. The residue from evaporation of the extract was shown to contain sodium chloride, but not a trace of parasulphobenzoic acid could be found.

6. *Preparation from Parasulphaminebenzoic Acid.* — The fusible diamide has also been prepared by reverse process, from

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[1] This dissertation, page 17. [2] This dissertation, page 11.

its intermediate saponification product, the same substance indeed that produces the infusible diamide.

Potassium parasulphaminebenzoate is triturated with an equal molecular quantity of phosphorus pentachloride, when reaction sets in with liquefaction of the mass. Allow the whole, when cooled, to remain for an hour over anhydrous ether. The ether solution is then filtered into a dry flask and dry ammonia passed in to saturation. After evaporation of the ether and treatment of the residue with water, ammonium chloride of course dissolves, but a considerable amount of substance is insoluble. This is filtered, washed, and crystallized from hot water. The substance is then found to have the crystalline form of the fusible diamide and to melt at 230.° It gives off ammonia on boiling with sodium hydroxide solution and on acidifying there is precipitated parasulphaminebenzoic acid, which was identified by its melting-point, about 280°, and by the formation of a soluble barium salt. The above process may be expressed by the following

equations: $p\text{-}C_6H_4\Big\langle\begin{matrix}COOK\\SO_2.NH_2\end{matrix} + PCl_5 = C_6H_4\Big\langle\begin{matrix}CO.Cl\\SO_2.NH_2\end{matrix} + KCl + POCl_3$

$$C_6H_4\Big\langle\begin{matrix}CO.Cl\\SO_2.NH_2\end{matrix} + 2NH_3 = C_6H_4\Big\langle\begin{matrix}CO.NH_2\\SO_2.NH_2\end{matrix} + NH_4Cl$$

It was only after many experiments that the above method was found to be the only successful one. At first the product from the action of the pentachloride was treated with water, and the insoluble material, after filtering and washing, was treated with strong ammonia, when the whole of it quickly dissolved. The ammonia was boiled off and the solution acidified. The precipitate formed melted at 280° and dissolved completely in sodium carbonate. Evidently, the chloride, $p\text{-}C_6H_4\Big\langle\begin{matrix}CO.Cl\\SO_2.NH_2\end{matrix}$ which the successful process proves to be formed, is at once broken down by water and ammonia to the original acid:

$$p\text{-}C_6H_4\Big\langle\begin{matrix}CO.Cl\\SO_2.NH_2\end{matrix} + H_2O + 2NH_3 = C_6H_4\Big\langle\begin{matrix}COONH_4\\SO_2.NH_2\end{matrix} + NH_4Cl$$

7. Corroborative Preparation of Parasulphaminebenzoic Ether.— The mass resulting from triturating potassium parasulphaminbenzoate with phosphorus pentachloride, was also extracted with boiling alcohol. Only potas-

chloride remained behind. The solution was evaporated to dryness and the residue crystallized from hot water. Two distinct kinds of crystals were seen. The whole was therefore neutralized with barium carbonate, evaporated to dryness, and extracted with alcohol. The extract was evaporated and the residue crystallized from hot water. This time, only long, slender needles, were seen. These melted at 94°, reproduced parasulphaminebenzoic acid on saponification and were in every way identical with the ethyl ether[1] of this acid, as shown by comparison with a known specimen. The barium salt left by extraction of the ether, was shown by analysis to be that of the [illegible]

0.095 gram lost 0.0138 gram H_2O at 160° and gave 0.0347 gram $BaSO_4$.

	Calculated for $(C_6H_4<^{COO}_{SO_2NH_2})_2Ba\,3H_2O$	Found
H_2O	14.35	14.52
Ba	21.85	21.48

Apparently, potassium parasulphobenzoate is not wholly acted upon by one equivalent of phosphorus pentachloride, but a part is converted into parasulphaminebenzoic

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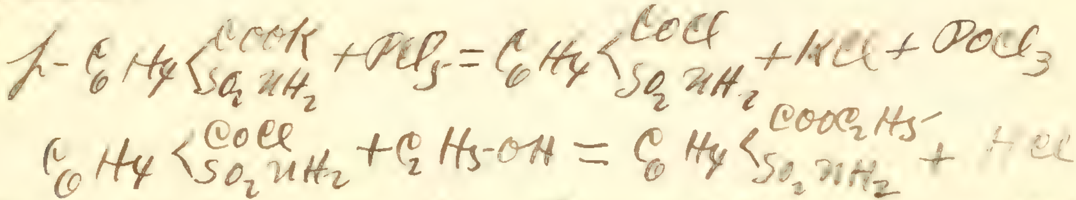
[1] Annalen, 178-288.

chloride, which is converted by alcohol into the corresponding ether:



$$p\text{-}C_6H_4\left\langle\begin{matrix}COOK\\SO_2NH_2\end{matrix}\right. + PCl_5 = C_6H_4\left\langle\begin{matrix}COCl\\SO_2NH_2\end{matrix}\right. + KCl + POCl_3$$

$$C_6H_4\left\langle\begin{matrix}COCl\\SO_2NH_2\end{matrix}\right. + C_2H_5\text{-}OH = C_6H_4\left\langle\begin{matrix}COOC_2H_5\\SO_2NH_2\end{matrix}\right. + HCl$$

8. Probable Preparation from Parasulphaminebenzoic Ether.—

The fusible diamide has thus been connected with parasulphaminebenzoic acid and its ether through its chloride. It only remained to establish direct connection between the ether and the diamide. A quantity of the ethyl parasulphaminebenzoate was prepared by the usual method, and shown to be identical with the beautiful substance described by Remsen[1]. Some of it was treated with concentrated ammonia, by the usual method of obtaining amides from ethers. Immediate solution resulted, and when the excess of ammonia was boiled off, the precipitate obtained by acidifying was found to be melt at 280° and to be fully soluble in sodium carbonate. Next, some of the ether was dissolved in absolute alcohol, the solution saturated

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[1] Annalen, 178-3[illegible]

with dry ammonia, and the whole heated in a sealed tube to 100° for a day, but the ether was regained unchanged. Finally, some of the dried ether was kept at 100° in a flask and dry ammonia passed over it, but no change was effected until the heat was raised to 170°, when decomposition set in. The mass charred a good deal, but it was treated with hot water, filtered, and the filtrate evaporated to crystallization. Needles melting at 94° were obtained. The mother-liquor from these was evaporated and there was obtained a small amount of colored crystals, that gave off ammonia with alkali, were of neutral reaction and melted at about 230°. The experiment was repeated with no increased yield of the latter product, which has the properties of the fusible diamide and whose probable formation may be thus represented.

$$p\text{-}C_6H_4\left<\begin{matrix}COOC_2H_5\\SO_2NH_2\end{matrix}\right. + NH_3 = C_6H_4\left<\begin{matrix}CO.NH_2\\SO_2.NH_2\end{matrix}\right. + C_2H_5\text{-}OH$$

But the ether is with difficulty affected by ammonia, except in presence of water, when, like the chloride[1],

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[1] This dissertation, page 32.

it is saponified:

$$p\text{-}C_6H_4\left\{\begin{array}{l}COOC_2H_5\\SO_2NH_2\end{array}\right. + NH_3 + H_2O = C_6H_4\left\{\begin{array}{l}COONH_4\\SO_2NH_2\end{array}\right. + C_2H_5OH$$

This is very remarkable, considering the ease with which compound ethers in general pass over to the corresponding amides.

C. Comparison of the Two Diamides

Neither theory nor facts would foretell the formation of isomeric diamides of the same acid. The two substances here described are alike in analysis and saponification-product in presence of hydrochloric acid; that is, they are both derivatives of parasulphobenzoic acid and each has two ammonia residues in the molecule. The most striking difference is found in their conduct toward dilute sodium hydroxide. The fusible diamide loses half, and the infusible, all, of the nitrogen, the former even much more rapidly

1. Constitution of the Fusible Diamide.—One of the first things that becomes apparent is that the fusible compound is the real or ordinary diamide of para-

sulphobenzoic acid, containing a carbamine and a sulphamine grouping. The compound is in every way like an ordinary amide, beautifully crystallized, fusible, soluble in alcohol and hot water, difficultly in cold. It shows that it contains a carbamine grouping by the fact that it gives off ammonia and passes over to parasulphaminebenzoic acid, which unquestionably contains a sulphamine grouping. Moreover, on saponification, it behaves exactly like its isomer, metasulphobenzoic diamide. Indeed, Limpricht and Uslar[1] discovered metasulphaminebenzoic acid by the saponification of the meta diamide with alkali. The fact that the fusible diamide can be regenerated from parasulphaminebenzoic acid probably through the ether and certainly through the chloride, from which also the ether may be prepared, leaves no room for doubt as to the nature of the fusible diamide, whose whose constitution would be represented by the formula, $p\text{-}C_6H_4\left(\begin{matrix}CO.NH_2\\SO_2.NH_2\end{matrix}\right.$

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[1] Annalen, 106-38

2. Discussion of the Infusible Diamide. — The nature of this compound is not as yet understood. No hypothesis as to its constitution has as yet suggested itself that is not open to serious objections. It may be well, however, to review the facts developed in its study: It gives off all of its nitrogen on standing in alkaline solution[1], and therefore if it contains the sulphamine grouping, that grouping here acts in a way never before known. A search through the literature showed no sulphamide that gives of ammonia even on boiling in alkaline solution. Experiments with parasulphaminebenzoic acid and paratoluenesulphone amide verified this conclusion. On the other hand, the carbamine grouping of the fusible diamide seems to require about two months[2] for complete saponification at about 0°. It would thus seem to be indicated that this grouping either is not contained in the infusible diamide or is there rendered much less stable towards alkalies.

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[1] This dissertation, page 21. [2] This dissertation, page 28.

The most striking conclusion impressed upon the worker is that the two nitrogen atoms in the infusible diamide act as if they existed under the same conditions. What is true of one appears to be true of the other; all of the nitrogen is given off or none at all. For example, a weighed quantity of the substance was treated with just half the quantity of potassium hydroxide solution necessary to saponify it completely. The result was that part of the diamide was unchanged, while the rest was fully saponified, the characteristic acid barium parasulphobenzoate being prepared from the product. Further, all attempts to obtain an intermediate product of saponification, such as the fusible diamide readily gives,[1] have failed. Caustic alkali completely decomposes it even at temperatures below 0°.[2] Its sulphuric acid solution, heated near its boiling point, changes in the same way, as shown by obtaining acid barium parasulphobenzoate from

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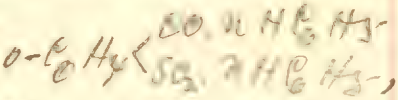
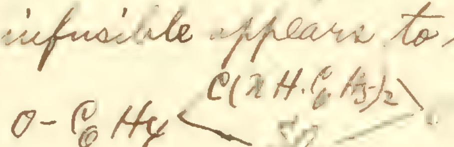
[1] This dissertation page 27. [2] This dissertation page 21.

the product. In other respects the infusible diamide is a very stable compound.[1]

It has not been found possible to change one diamide into the other. The fusible substance was heated for some time just above its melting point, but no trace of its isomer could be detected in the badly-charred products. Some of the infusible substance was heated with water in a sealed tube, but no transformation could be noted.

The only analogy known for such isomeric ammonia derivatives is in the case of the two isomeric dianilides of orthosulphobenzoic acid,[2] one being fusible, the other infusible. The fusible substance has been shown to be the real or ordinary diamide,  $o\text{-}C_6H_4\left<\substack{CO.NHC_6H_5\\SO_2.NHC_6H_5}\right.$, while the infusible appears to have the unsymmetrical formula,  $o\text{-}C_6H_4\left<\substack{C(NH.C_6H_5)_2\\SO_2}\right>O$. The infusible dianilide is, however, a remarkably stable substance, undecomposible by boiling sodium hydroxide solution. The infusible parasulphobenzoic diamide is thus

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[1] This dissertation, page 16. [2] Am. Ch. Journ. 17-310-341, and Coale's and Roberts' Dissertations, Johns Hopkins University

quite unlike it in this respect,[1] and further, the anhydride condition between substituting acid residues of the para series is unknown, though paradiazobenzenesulphonic anhydride, $p\text{-}C_6H_4{<}\genfrac{}{}{0pt}{}{N_2}{SO_2}{>}O$, is easily formed.

Products from the Heated Mass that are Soluble in Water

A. Process of Separation

The filtrates from the specimens of the infusible diamide,[2] obtained by heating parasulphaminebenzoic acid to 220°-235°, were collected and boiled for some time with purified animal charcoal. The filtered solution was evaporated to crystallization, the mother-liquor from this first batch of crystals further evaporated, and this process continued until six successive batches were obtained. The residue from the last was evaporated to dryness. The first three batches were found to be alike. The last three were small in amount, but appeared to consist chiefly of an acid that formed an insoluble

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[1] This dissertation, page 19. [2] This dissertation, page 11.

barium salt which crystallized in fine, voluminous needles. The residue contained practically no ammonia. Three different substances were thus detected and these will be successively considered.

In the process of heating parasulphaminebenzoic acid[1], there is formed on the watchglass two sublimates, one an amorphous coating, the other glancing needles jutting out from the glass. Both are very soluble in water. They were separated mechanically, and the former was found to contain ammonia, while the latter apparently did not. Not enough of either was obtained for further study.

B. Acid Ammonium Parasulphobenzoate

The first three batches consisted of this salt, being the chief soluble product of the heated mass. For comparison, acid ammonium parasulphobenzoate was made by two distinct known methods. First, the sulphamine group of parasulphaminebenzoic acid[2] was saponified by heating with hydrochloric acid

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[1] This dissertation, page 5.

[2] Am. Ch. Journ. [illegible]

in a sealed tube to 200°:

$$p\text{-}C_6H_4<^{COOH}_{SO_2NH_2} + H_2O = C_6H_4<^{COOH}_{SO_2ONH_4}$$

Next, according to Hartmann's process, the nitrile of paracyanbenzenesulphone chloride[1] was saponified by a similar heating at 150°:

$$p\text{-}C_6H_4<^{CN}_{SO_2Cl} + 3H_2O = C_6H_4<^{COOH}_{SO_2ONH_4} + HCl$$

The two specimens thus prepared were, as we should expect, alike in all respects, and identical with the three batches on hand and with the specimen obtained from the heating at 235°.[2] The solutions of all six specimens gave long, transparent, rhombic plates, that were strongly acid, contained ammonia, lost water under the same conditions, and with barium chloride gave silky precipitates. These six precipitates, on recrystallization, appeared in the long needles that identified them as acid barium parasulphobenzoate. This comparison shows that the salt obtained as the chief soluble product from every heating of parasulphaminebenzoic acid is acid ammonium parasulphobenzoate

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[1] Dissertation, page 18.

[2] This dissertation, page 6.

It is judged from experience that about 40 per cent of the acid heated at 220° goes over into this salt, calculated as dehydrated.

C. Excess of Free Parasulphobenzoic Acid

The residue from the six batches was very acid and contained practically no ammonia. Yet on testing its solution with barium chloride, a silky precipitate precipitate was obtained in quantity, which on crystallization showed the same long needles of acid barium parasulphobenzoate as obtained from the first three batches. The result of analysis was:

0.206 gram salt lost 0.019 gram H_2O at 200° and gave 0.08 gram $BaSO_4$.

	Calculated for $(C_6H_4<^{COOH}_{SO_3})_2Ba.3H_2O$	Found
H_2O	9.11	9.22
Ba	23.10	22.79

It has already been shown that when parasulphaminebenzoic acid is heated to 220°-235°, varying amounts[1] of the infusible diamide are formed, depending on the temperature, but that the first sub-

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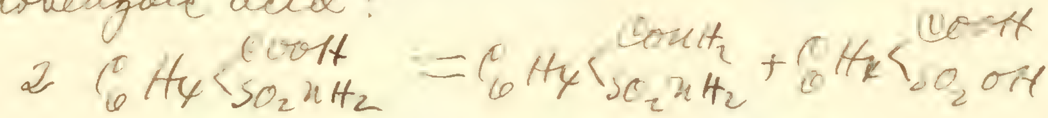
[1] This dissertation, page 11.

ble in water retain the original acidity unchanged[1] Since the formation of acid ammonium parasulphobenzoate and the isoparasulphaminebenzoic acid[2] does not alter the acidity, and since there has been removed from the solution varying amounts of neutral diamide, this constancy of acidity can only be explained by supposing the equivalent formation of free parasulphobenzoic acid:



$$2\ C_6H_4<^{COOH}_{SO_2NH_2} = C_6H_4<^{CONH_2}_{SO_2NH_2} + C_6H_4<^{COOH}_{SO_2OH}$$

Thus by two different methods this reaction has been corroborated.

D. Isoparasulphaminebenzoic Acid

Efforts were made to isolate the acid of the last three batches by a better method. It was found that if the mass obtained from heating parasulphaminebenzoic acid to 220° for eight hours, is pulverized and extracted with hot alcohol the filtrate will deposit a flocculent precipitate on cooling. This precipitate was filtered off, washed with alcohol

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[1] This dissertation, page 12. [2] See below.

pressed dry, and examined. It was found to be neutral to contain ammonia, and to give with barium chloride the same insoluble salt as obtained from the last three batches.

1. Analysis.— The barium salt was recrystallized from hot water, analyzed and found to contain an acid isomeric with parasulphaminebenzoic acid.

I. 0.2182 gram salt lost 0.0137 gram H_2O at 150°; 0.0202 gram H_2O at 200° and gave 0.086 gram $BaSO_4$.

II. 0.1916 gram salt gave 8.2 cc. of nitrogen at 18° and 755.45 mm

III. 0.1342 gram salt gave 0.103 gram $BaSO_4$ (Carius)

	Calculated for $\left(C_6H_4{}^{COO}_{SO_2NH_2}\right)_2Ba.3H_2O$	I	II	III
$2H_2O$	6.09	6.28		
$3H_2O$	9.13	9.21		
Ba	23.18	23.17		
N	4.73		4.86	
S	10.82			10.54

2. Properties.— The free acid was found to be very soluble

in water. Its salts were studied with a view to analysis, but none of them, except those of barium and ammonium were at all well-characterized. The latter salt, which is obtained in the first instance, crystallizes in short, stout, transparent prisms, quite different from the glistening aggregates of needles of the ammonium parasulphaminebenzoate[1] The calcium, strontium, zinc, magnesium, and lead salts of the two acids were made and compared side by side. Those of the parasulphaminebenzoic acid were very well-defined, the zinc salt being specially beautiful, while those of the iso acid were in each of the five cases, non-crystallizable and all, except the lead salt, very soluble. No concordant results could be obtained in the analysis of the latter, which when dry caked up into small hard scales. The mercury salt was soluble, but on boiling the solution there was precipitated a white powder, probably a mercurammido-derivative. A good quantity of the silver salt was

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[1] Annalen, 178-303.

filtered and slowly evaporated in a dark place. A gray powder resulted that did not give concordant results on analysis.

3. Purification of the Barium Salt. — Parasulphamine-benzoic acid is heated to 220° for eight hours, and the resulting mass, after being pulverized, is shaken up in an Erlenmeyer flask with about ten times its weight of boiling-hot alcohol. The alcohol is filtered after about fifteen minutes, and evaporated to about one-fourth its original volume. The flakes that separate out, on cooling, are filtered, and dissolved in water without drying; the resulting solution is made slightly alkaline with ammonia and barium chloride is added. The precipitate obtained is washed well on a filter and recrystallized from hot water, being then pure. The residue from the alcohol extract above is next treated with water, without drying, and the infusible diamide filtered off. The filtrate is here also rendered slightly alkaline with ammonia, when by

addition of barium chloride a large precipitate appears. This is washed on a filter, dissolved in boiling water and boiled for an hour with three times its weight of animal charcoal. The filtered solution deposits the colorless salt on cooling, identical in properties with the one obtained from the alcohol as above analyzed. Including both specimens, a yield of about ten percent is obtained, calculated as free acid.

4. *Properties of the Barium Salt.*— It crystallizes, on cooling from hot water solution, in exceedingly fine needles that are so intricately interwoven throughout the liquid, that when the salt comes out of saturated solution, the containing vessel may be inverted without loss of material, though only about one percent of salt was in solution. It is slightly soluble in cold water, unaffected by even strong ammonia, but very soluble in even dilute acid.

5. *Saponification with Alkali.* — A quantity of barium isoparasulphaminebenzoate was heated with

potassium hydroxide solution in a silver crucible over a very small flame. Ammonia did not begin to come off until almost all of the water had been boiled away and the resulting mass would solidify upon cooling. Just as soon as moistened litmus showed that all ammonia was off, the flame was withdrawn, and the cooled mass treated with water, filtered from barium carbonate and acidified. Sulphur dioxide was then evolved in quantity. By the usual method of extraction with ether, crystals of an acid nature were obtained that were identical in form, solubility and melting-point, 210°, with paroxybenzoic acid[1]. They were also identified by the fact that they gave off a gas at 220° and passed over to phenol, as detected by its odor and its tribrom derivative. The above transformations are thus expressed:

$$p\text{-}C_6H_4\left\langle\begin{matrix}COOH\\SO_2NH_2\end{matrix}\right. + 3KOH = C_6H_4\left\langle\begin{matrix}COOK\\OH\end{matrix}\right. + K_2SO_3 + NH_3 +$$

$$C_6H_4\left\langle\begin{matrix}COOH\\OH\end{matrix}\right. = C_6H_5.OH + CO_2$$

<u>6. Saponification with Acid.</u>—Some of the barium

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[1] Annalen, 178-275

salt was also heated with hydrochloric acid in a sealed tube to 270°. After all free acid was evaporated from the product, it was dissolved in boiling water, the barium exactly precipitated, and the filtrate allowed to cool. There then appeared a very small quantity of a substance in flaky form. This was very soluble in hot water, insoluble in cold, soluble in alcohol. It was an acid and when precipitated appeared always in flaky form. It sublimed without melting. At first, it was thought to be the same substance as that obtained by a similar treatment of the infusible diamide! But the latter was insoluble in hot water, and when precipitated appeared in milky form. Both are acid and sublime without melting.

Almost the whole product of the saponification is soluble in cold water. Half of the filtrate from the trace of substance just described was neutralized with barium carbonate and filtered; then the two halves were brought together and evaporated to crystallization, when there appeared the long needles of acid barium

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[1] This dissertation [illegible]

parasulphobenzoate, an analysis of which gave:

0.164 gram lost 0.015 gram H_2O at 200° and gave 0.0638 gram $BaSO_4$

	Calculated for $(C_6H_4 < {}^{COOH}_{SO_2O})_2 Ba . 3H_2O$	Found
H_2O	9.11	9.14
Ba	23.10	22.81

The result of this saponification may be thus expressed:

$$p\text{-}C_6H_4 < {}^{COOH}_{SO_2NH_2} + H_2O = C_6H_4 < {}^{COOH}_{SO_2ONH_4}$$

7. Attempt to Prepare the Sulphinide. — It would evidently be important to ascertain what sulphinide corresponds to isoparasulphaminebenzoic acid. In order to learn this, dried potassium isoparasulphaminebenzoate was ground thoroughly with an equivalent molecular amount of phosphorus pentachloride, and the mass warmed gently. Reaction easily occurred and on subsequent addition of water, there separated a white insoluble substance. This was filtered, washed and on examination found to be free from phosphorus and to contain chlorine. It was utterly insoluble in every solvent tried and thus quite

different from ordinary acid chlorides. On boiling in alkali, solution took place, and on acidifying and cooling, no insoluble substance appeared, but the solution, rendered slightly alkaline with ammonia, gave with barium chloride a precipitate that on crystallization from hot water, showed the fine, voluminous needles of barium isoparasulphaminebenzoate. This peculiar substance, thus shown to be a chloro-derivative of the iso acid, dissolves at once in cold concentrated or hot dilute ammonia. When excess of acid is added to either solution, there is precipitated a jelly-like mass that reminds one, before and after attempted filtration, very much of aluminium hydroxide obtained in the cold. The substance was found to be insoluble in all solvents tried.

8. Discussion of Isoparasulphaminebenzoic Acid.—The close relation of this substance to parasulphaminebenzoic acid is shown by the fact that both give not only the same product when saponified with acid,[1] but also the same by alkaline saponification. The iso acid

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[1] This dissertation, page 50, and Am. Ch. Jour. 1-856

may be paracarbaminebenzenesulphonic acid, $p\text{-}C_6H_4<^{CONH_2}_{SO_3H}$ but the fact that it gives off no trace of ammonia on boiling with dilute sodium hydroxide[1] would seem to argue against this view. On the other hand, the acid is very soluble in water, like the sulphonic acids, and like many of these, forms a difficultly soluble barium salt. In this connection, it may be mentioned that Limpricht and Uslar[2], in their study of metasulphaminebenzoic acid, isolated two iso acids, one very soluble in water, the other amorphous. They succeeded in transforming the amorphous into the ordinary acid by heating in a sealed tube to 170°-180°. A similar experiment was tried with free isoparasulphaminebenzoic acid, but no change could be detected.

Discussion of the Influence of Heat on Parasulphaminebenzoic Acid.

It has been shown[3] that when parasulphaminebenzoic acid is heated for a short time at its melting-point, almost the entire product, not carbonized,

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[1] This dissertation, page 41. [2] Annalen, 110-113.

[3] This dissertation, page 8.

is acid ammonium parasulphobenzoate, and that at lower temperatures, where the reaction is cleaner, about 40 percent of this salt is formed. It is evident that when parasulphaminebenzoic acid is heated, the tendency is to take up water and pass over to the acid ammonium salt by saponification:

$$p\text{-}C_6H_4\left\{\begin{matrix}COOH\\SO_2NH_2\end{matrix}\right. + H_2O = C_6H_4\left\{\begin{matrix}COOH\\SO_2ONH_4\end{matrix}\right.$$

Since there is evident carbonization at 285° and there is very little of any product besides the acid ammonium salt formed, the natural conclusion is that a part obtains the necessary water by the decomposition of the rest of the acid.

Such an inference could not be drawn from the heatings at 220°-255°; for very little carbonization is apparent, and it is found that quite a different reaction occurs. Infusible parasulphobenzoic diamide is always formed[1]. There is certainly some connection between the formation of this substance and the evident tendency of parasulphaminebenzo-

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[1] This dissertation, page 12

acid to take up water. It could hardly obtain the water from a substance so stable towards heat as the infusible diamide, but it might get it from the free parasulphobenzoic acid that is necessarily simultaneously formed. Possibly the diamide is only formed because it allows the formation of a substance that may be dehydrated. If this latter supposition be true, no diamide will be formed if parasulphamine and parasulphobenzoic acids are heated together.

1. Action of Parasulphobenzoic Acid on Parasulphaminebenzoic Acid.—A verification of the above view was obtained by the following experiment: Parasulphobenzoic acid was made by very carefully precipitating the barium from a pure specimen of its acid barium salt with just enough sulphuric acid, evaporating the filtered solution to dryness and drying the product at 130°. This was mixed with an equal weight of parasulphaminebenzoic acid

also dried, and the mixture was ground thoroughly, placed in a small evaporating dish and allowed to remain at a temperature of about 223° for eight hours. It was then taken out, cooled, and on letting stand with water, was found to have completely dissolved. The solution was evaporated to successive crystallizations, as in other similar cases[1], but nothing was obtained except acid ammonium parasulphobenzoate and free parasulphobenzoic acid. Certainly, no trace of infusible diamide was formed.

This experiment apparently shows that parasulphobenzoic acid has in some way the power to give off water to parasulphaminebenzoic acid, and that, on treatment with water subsequently, the product, whatever it is, has the power to pass back to parasulphobenzoic acid. There is here indicated a probable cause for the formation of the infusible diamide, which may be stated thus: On account of the tendency of parasulphaminebenzo

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[1] This dissertation, page 41.

acid to take up water and pass over to acid ammonium parasulphobenzoate, infusible parasulphobenzoic diamide is formed, in order that there may occur the consequent formation of free parasulphobenzoic acid, which has been shown to have the power to furnish the necessary water[1]. This reaction would be represented thus:

$$3\,C_6H_4\begin{cases}COOH\\SO_2NH_2\end{cases}=C_6H_4\begin{cases}COOH\\SO_2ONH_4\end{cases}+C_6H_4\begin{cases}CONH_2\\SO_2NH_2\end{cases}+C_7H_4SO_4$$

The expression $C_7H_4SO_4$ only represents the dehydrated condition that must be inferred when parasulphobenzoic acid, without itself suffering material change, causes the saponification of parasulphaminebenzoic acid.

2. Percentage of Products Formed.— According to the above hypothesis, about 33 percent each, of salt, of amide, and of dehydrated acid, could be formed when the sulphamine acid is heated. As a matter of fact, under the lowest possible temperature of reaction so far obtained, only 23 percent of diamide

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[1] This dissertation, page 11.

is formed, while about 40 percent of acid ammonium parasulphobenzoate is obtained[1]. This, taken with the fact that the higher the temperature, the less diamide is formed, seems to justify the conclusion that the ideal reaction would give 33 percent of this product, and that even at 220°, the lowest temperature available for action, about 30 percent of the sulphamine acid is changed by other transformations, partly by formation of the iso acid,[2] and partly by the carbonization[3] that takes place at 285°. It is judged, therefore, that when parasulphaminebenzoic acid is heated to 220° for eight hours, it is changed about as follows.

Substances Formed	Percent
Infusible parasulphobenzoic diamide,	23
Acid ammonium parasulphobenzoate,	23
Free parasulphobenzoic acid,	23
Isoparasulphaminebenzoic acid,	10
Acid ammonium parasulphobenzoate and carbonized products, like those found at 285°,	21
	100

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[1] This dissertation, page 43. [2] This dissertation, pages 45.
[3] This dissertation, page 8.

3. Shifting of the Nitrogen Atom.—Three fundamental reactions have been found to take place when para-sulphaminebenzoic acid is heated:

(1) $p\text{-}C_6H_4<^{COOH}_{SO_2NH_2} + H_2O = C_6H_4<^{COOH}_{SO_2ONH_4}$

(2) $2\ p\text{-}C_6H_4<^{COOH}_{SO_2NH_2} = C_6H_4<^{CONH_2}_{SO_2NH_2} + C_6H_4<^{COOH}_{SO_3H}$

(3) $p\text{-}C_6H_4<^{COOH}_{SO_2NH_2} = iso\text{-}C_6H_4<^{COOH}_{SO_2NH_2}$

Since the incentive to this investigation was the possibility of noting any shifting of nitrogen similar to that observed by Hartman, the above transformations were considered from that standpoint. The first reaction does not give assistance, because the position of the base in the acid sulphobenzoates depends on the comparative avidity of the acid groupings, so that if the ammonium were first united to the weaker grouping, it would on treatment with water change to the stronger. In the third reaction, shifting may have taken place, but is not proven, because the ammonia residue in the iso acid acts in all respects like that in

its more common isomer.[1] But in the second case, there is every probability that at least part of the nitrogen has shifted from union with sulphur to union with carbon. Indeed, both nitrogen atoms of the infusible diamide act as if they were not in a sulphamine grouping. At all events, it appears very probable that when parasulphaminebenzoic acid is heated to 220°-235°, a portion of the nitrogen shifts from union with sulphur to union with carbon and this seems to corroborate the facts developed by Hartman.

Limpricht and Uslar[2] in their description of metasulphaminebenzoic acid, mention incidentally that this substance, which is very similar to the para acid, darkened when kept at about its fusing point for some time and passed over to a product that was easily soluble in water. It would be interesting to ascertain whether reactions here occur similar to those noted.

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[1] This dissertation, page 53.   [2] Annalen, [illegible]

in the foregoing pages.

II. The Action of Phosphorus Pentoxide on Parasulphaminebenzoic Acid

With a view to ascertaining whether this reagent had any dehydrating action on parasulphaminebenzoic acid, or at least permitted any more decided shifting of nitrogen, equal weights of the two substances were heated together at about 230° for eight hours and the products studied. The great difficulty in this case was to get rid of the phosphorus after the operation. The heating had been carried on in an Erlenmeyer flask, protected from outside moisture and placed in a sulphuric acid bath. No diamide could be detected in the products. This corroborates the view already given of the reason for the formation of this substance; for in this case, the phosphorus pentoxide absorbs all water given off by fusion of the sulphamine acid and thus prevents the trans-

formation that takes place when the acid is heated alone.

III. Intermediate Product of the Action of Phosphorus Pentachloride on Parasulphaminebenzoic Acid

In his fundamental reaction,[1]

$$p\text{-}C_6H_4\left\langle{}^{COOH}_{SO_2NH_2}\right. + 2PCl_5 = C_6H_4\left\langle{}^{CN}_{SO_2Cl}\right. + 2POCl_3 + 3HCl$$

Hartmann found that action took place in two stages, at 60° and at 150°, phosphorus oxychloride being given off at each stage, and that only at the second stage was the paracyanobenzenesulphone chloride formed. Hartmann attempted to isolate products from the liquid that resulted after the first stage, and mentions that a product melting at about 80° was obtained from benzene, but presumably in quantity not large enough for study.

Process for Obtaining the Intermediate Phosphochloride

An attempt was made to purify the product by extracting with ligroïn and this was successful. The method of procedure was as follows:

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[1] Dissertation, pages 7 and 9.

10 grams of dried para-sulphaminebenzoic acid and 21 grams of phosphorus pentachloride are thoroughly triturated in a dry mortar, and quickly brought into a dry 750 cc. Erlenmeyer flask, which is then kept free from atmospheric moisture by connection with a small U-tube containing a little sulphuric acid. The flask is clamped in position in a sulphuric-acid bath, and the temperature is gradually raised. When, at about 60°, reaction sets in, the flask is raised above the bath until evolution of hydrochloric acid ceases; then is lowered again, raised again, and so on, until action at 60° is complete. The heat is then raised slowly to 110°, with occasional shak- of the flask, and kept there until no more oxychloride collects in the U-tube and the liquid in the flask is transparent. The flask is then slowly allowed to cool and about 200 cc. of dry ligroin is added. The whole is now vigor-

ously shaken for a few minutes. The clear, yellow oil soon solidifies to a beautiful mass of crystals, while the ligroïn, which is poured off, is found to contain phosphorus and chlorine. 500 cc. of fresh ligroine is now poured into the flask, which is then immersed in water kept at 70°. The mass again becomes oily, as the temperature rises, and is constantly stirred up into the ligroïn with a glass rod. When the ligroïn has reached 70°, it is kept there five minutes and then is filtered off on a dry fluted filter, and a dry funnel into a dry 500. cc. Erlenmeyer flask. The latter is well stoppered and allowed to stand from 12 to 24 hours, when it is found to contain a considerable quantity of very beautiful, transparent, stout prisms that often attain a length of an inch.

Care must be taken to let the reaction at 60° proceed as slowly as possible and especially not

to heat the ligroïn above 70°. To this end, it is best to mix a high-boiling with about one-fourth its volume of a low-boiling ligroïn, and distil the product until a residue is obtained boiling at 70°. If the heating is carried much above this temperature, there are formed, even with a purified ligroïn, dark, oily products that become hopelessly intermingled with the clear crystals.

The ligroïn over the crystals is well stirred and poured off, carrying with it lighter products containing less valonine. Fresh ligroïn is added several times and the lighter products thus fully poured off. The clinging crystals are then detached from the glass, and all are poured into a beaker under ligroïn and carefully examined. Every dark piece present is withdrawn. The clean product is then thrown on a filter, washed with fresh ligroïn, quickly and well pressed out on drying paper, and placed in a vacuum-

acid desiccator.

Analysis of the Phosphochloride

A qualitative test showed that the substance contained phosphorus and chlorine. Analysis led to the empirical formula, $C_7H_4NO_3SPCl_4$, which corresponds to $p\text{-}C_6H_4\left\langle\begin{matrix}CO.Cl\\SO_2.N{:}PCl_3\end{matrix}\right.$

I. 0.287 gram gave 0.0408 gram H_2O and 0.2528 gram CO_2.
II. 0.2914 gram gave 0.0385 gram H_2O and 0.255 gram CO_2,
III. 0.4006 gram gave 15 cc. of nitrogen at 23° and 760.55 mm.
IV. 0.4128 gram gave 16.3 cc. of nitrogen at 26° and 761 mm.
V. 0.2439 gram gave 0.168 gram $BaSO_4$ (Carius).
VI. 0.4472 gram gave 0.1412 gram $Mg_2P_2O_7$
VII. 0.363 gram gave 0.562 gram AgCl
VIII. 0.2887 gram gave 0.4502 gram AgCl

	Theory	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	By Differ-
C	23.69	24.02	23.93							
H	1.13	1.58	1.47							
N	3.95			4.22	4.37					
O	13.53									13.48
S	9.03					9.46				
P	8.74						8.81			
Cl	39.92							38.35	38.54	

Chlorine was determined by placing about 0.2 gram in 400 cc. of water, warming until dissolved, and weighing as silver chloride. Phosphorus was determined by placing about 0.2 gram in 100 cc. of water, heating to boiling, filtering off the parasulphaminebenzoic acid that separates out on cooling, and precipitating from the filtrate as ammonium magnesium phosphate.

Phosphochloroparasulphaminebenzoic Chloride

The above analyses of this compound, the reasons for the naming of which will be given later[1], are not very close to the theory, because of the extreme instability of the substance and consequent difficulty of purification. It absorbs moisture from the atmosphere with great avidity, giving off fumes of hydrochloric acid. The specimens analyzed above for chlorine were made from different heatings and were in both cases protected from moisture as much as possible; yet

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[1] This dissertation, page 73

the figures come about 1½ percent too low, some hydrochloric acid being perceptibly given off in the process of pressing dry. The loss of chlorine of course increases the percentages of the other elements, by probable substitution of hydroxyl in its place. Further, the presence of traces of the darker products, that must be mechanically separated, is not improbable.

The compound has such a tendency to absorb water, give off hydrochloric acid and become liquid that it cannot be pressed dry with filter paper except on a dry day. Under conditions of greater atmospheric humidity, the substance attracts water faster than the paper can absorb the resulting thick liquid. The substance crystallizes beautifully from ligroin in transparent prisms that are not truncated by any well-defined faces. When exposed to the air, the crystals quickly whiten. They break up in water,

dissolving quickly, if warm, and the solution deposits parasulphaminebenzoic acid on cooling. This acid, as here obtained, is the purest specimen dealt with in the present work, crystallizing beautifully in glancing, short needles, fusing sharply at 285°, and forming a soluble barium salt of very pure appearance. The phosphochloride melts at 82° and is soluble in benzene, but from the solution no well-defined crystals were obtained.

Further Treatment of the Intermediate Mass

If the mass remaining after the extraction of the phosphochloride is successively extracted with fresh ligroin each successive batch that separates out on cooling contains less chlorine than the preceding one, and all pass to parasulphaminebenzoic acid on treatment with water. Thus, 38.35, 37.00, 32.89, and 30.07 were the results obtained by analyses of four successive extracts, no more being obtainable from the residue. The [illegible]

product, containing 30.07 per cent of chlorine, was found to be identical with that obtained by treating the phosphochloride with ligroin at 70°, when phosphorus oxychloride was extracted, about one fourth of the substance dissolved, and there separated from the filtrate, on cooling, a substance that gave 30.14 per cent of chlorine on analysis and was identical in appearance with that giving 30.07 per cent. It was very difficultly soluble, only about 0.2 gram separating from a liter of ligroin, and consisted of silky hairs that looked very much like the best cotton fiber. It contained no trace of phosphorus; for 0.1128 gram of it gave no ammonium magnesium phosphate.

If the same ligroin, containing phosphorus oxychloride and hydrochloric acid, was used for the successive extracts, there was finally obtained a substance that separated in long

slender, arborescent aggregations, of very beautiful appearance. These broke up completely on the slightest agitation, and could not be pressed dry for analysis. If the ligroïn from the phospho-chloride crystals was filtered into a wet vessel, there gradually separated a quantity of fine needles

Influence of Heat on Phosphochloroparasulphaminebenzoic Chloride

A quantity of the purified substance was placed at the bottom of a tube, fused at one end, and arranged to rest in a sulphuric-acid bath. Not far from the substance, the tube was bent into two successive U-forms, the one nearest the substance being arranged to dip under water, and the other U-bend being moistened with sodium hydroxide solution. Beyond this latter, the tube was drawn out to a coarse capillary, and broken about two inches from the widening.

The bath was now heated slowly. The

phosphochloride melted sharply at 82° and began to give off vapors at 140°. The temperature was gradually raised to 200° and kept there until no more gas was evolved. The mass had blackened considerably, a yellow substance in the form of clear needles had sublimed just above the bath, and a liquid had collected in the U-bend nearer the bath. The tube was broken at each end of this bend, and the three parts examined. The more distant U-bend, on addition of excess of sulphuric acid, gave off sulphur dioxide. The liquid in the nearer U-form was transferred to cold water, when it settled to the bottom as an oil, but gradually dissolved. The solution was found to contain considerable quantities of hydrochloric and phosphoric acids, altogether unquestionable indications of phosphorus oxychloride.

The tube containing the charred residue and

the sublimate was broken up into fragments, extracted with benzene, and the filtered extract evaporated to dryness. The residue thus obtained was placed in a distilling bulb, water added, and half of the liquid distilled over into another vessel. The distillate contained a white substance that had a very decided nitrile odor, was very volatile with watery vapor, and melted at 93°. These properties correspond exactly with parachlorbenzoic nitrile.[1]

The liquid remaining in the distilling-bulb was filtered and then found to contain hydrochloric acid and a non-volatile acid. It was evaporated to dryness, the solution of the residue neutralized with barium carbonate, and the filtrate from this evaporated to crystallization. Seed-like crystals, corresponding to the description of barium paracyanbenzenesulphonate appeared. Since experiment had previously shown that paracyanbenzenesulphonic acid is fully saponified by evapo-

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[1] Hartman's Dissertation, page 25.

ration with concentrated hydrochloric acid, the barium was exactly precipitated from the above needlike salt, and the resulting filtrate evaporated three times with hydrochloric acid. The dried residue was then dissolved, half of the solution was neutralized with barium carbonate, and filtered, and the two halves brought together. Then, by evaporation of the liquid to crystallization, there appeared on cooling very characteristic, long needles of acid barium parasulphobenzoate. The transformations thus obtained from the substance remaining in the distilling bulb are identical with those obtained by Hartmann from paracyanbenzenesulphone chloride[1], and are considered as establishing the presence of this substance:

$$p\text{-}C_6H_4<\begin{matrix}CN\\SO_2Cl\end{matrix} \rightarrow C_6H_4<\begin{matrix}CN\\SO_2OH\end{matrix} \rightarrow C_6H_4<\begin{matrix}COOH\\SO_2OH\end{matrix}$$

Constitution of Phosphochloroparasulphaminebenzoic Chloride

Analysis shows the empirical formula of the substance to be $C_7H_4NO_3SPCl_4$. That the con-

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[1] Dissertation, pages 10 and 12.

pound is a derivative of parasulphaminebenzoic acid is shown by the fact that this acid crystallizes out on cooling its solution in hot water. That the phosphorus exists in the quinquivalent condition is shown by the fact its solution in cold water contains a considerable amount of phosphoric acid. These results could hardly be explained by other than the following equations;

$$p\text{-}C_6H_4\left\langle\begin{matrix}CO.Cl\\SO_2.N:PCl_3\end{matrix}\right. + 2H_2O = C_6H_4\left\langle\begin{matrix}COOH\\SO_2NH_2\end{matrix}\right. + HCl + POCl_3$$

$$POCl_3 + 3H_2O = H_3PO_4 + 3HCl$$

The products obtained by heating the substance corroborate this constitution. Further, an exact analogue has been obtained by the action of phosphorus pentachloride on benzenesulphone amide. Wichelhaus[1] gave the formula of the resulting compound as $C_6H_5.SO_2.NH.PCl_2$, but Wallach and Huth[2] later repeated his work and showed that the analysis and behavior of the substance indicated the formula, $C_6H_5.SO_2.N:PCl_3$ as correct. In the light of all these

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[1] Berichte, 2-502. [2] Berichte, 9-424.

facts, the substance herein described has been given the name phosphochloroparasulphaminebenzoic chloride.

Fuller Study of the Action of Phosphorus Pentachloride on Parasulphaminebenzoic Acid

It has been been shown[1] that the phosphochloride gives of phosphorus oxychloride and passes over to paracyanbenzenesulphone chloride, or gives off sulphurdioxide in addition and passes to parachlorbenzoic nitrile:

$$p\text{-}C_6H_4\Big\langle\begin{matrix}CO.Cl\\ SO_2.N:PCl_3\end{matrix} = C_6H_4\Big\langle\begin{matrix}CN\\ SO_2Cl\end{matrix} + POCl_3$$

$$p\text{-}C_6H_4\Big\langle\begin{matrix}CO.Cl\\ SO_2.N:PCl_3\end{matrix} = C_6H_4\Big\langle\begin{matrix}CN\\ Cl\end{matrix} + SO_2 + POCl_3$$

Hartman has already shown[2] that the former of these products gives off sulphur dioxide and passes over to the latter. This in addition to the above evidence, completes the proof that phosphochloroparasulphaminebenzoic Chloride is another intermediate product of the action of phosphorus pentachloride upon parasulphaminebenzoic acid.

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[1] This dissertation, page 73. [2] Dissertation, page 11.

$p\text{-}C_6H_4\Big\langle{}^{COOH}_{SO_2NH_2} \rightarrow C_6H_4\Big\langle{}^{CO.Cl}_{SO_2.N:PCl_3} \rightarrow C_6H_4\Big\langle{}^{CN}_{SO_2Cl} \rightarrow C_6H_4\Big\langle{}^{CN}_{Cl}$

The full reactions by which these substances are formed may be thus expressed:

(1) $p\text{-}C_6H_4\Big\langle{}^{COOH}_{SO_2NH_2} + 2PCl_5 = C_6H_4\Big\langle{}^{CO.Cl}_{SO_2N.PCl_3} + POCl_3 + 3HCl$

(2) $p\text{-}C_6H_4\Big\langle{}^{CO.Cl}_{SO_2.N:PCl_3} = C_6H_4\Big\langle{}^{CN}_{SO_2Cl} + POCl_3$

(3) $p\text{-}C_6H_4\Big\langle{}^{CN}_{SO_2Cl} = C_6H_4\Big\langle{}^{CN}_{Cl} + SO_2$

Hartman states that the second stage of the reaction takes place at about 150°, and the pure phosphochloride begins to decompose at 140°.

The new substance, thus defined as an intermediate product, does indeed give considerable in explaining the action of phosphoric pentachloride on parasulphaminebenzoic acid, but the intermediate transformation,

$p\text{-}C_6H_4\Big\langle{}^{CO.Cl}_{SO_2.N:PCl_3} \rightarrow C_6H_4\Big\langle{}^{CN}_{SO_2Cl}$

appears almost as deep-seated as it appeared when only the end-products,

$p\text{-}C_6H_4\Big\langle{}^{COOH}_{SO_2NH_2} \rightarrow C_6H_4\Big\langle{}^{CN}_{Cl}$

were known. It is now evident, however, that the hypothetical transformation,

$$p\text{-}C_6H_4 < \begin{matrix} COOH \\ SO_2NH_2 \end{matrix} \rightarrow C_6H_4 < \begin{matrix} CONH_2 \\ SO_2OH \end{matrix}$$

does not take place and that the shifting of nitrogen is accompanied by a simultaneous shifting of chlorine. It is difficult to conceive that any intermediate product is obtainable in the reaction,

$$p\text{-}C_6H_4 < \begin{matrix} CO.Cl \\ SO_2.N:PCl_3 \end{matrix} = C_6H_4 < \begin{matrix} CN \\ SO_2Cl \end{matrix} + POCl_3$$

so that probably all the steps of this reaction are now known.

General Summary of Results

1. No appreciable loss in weight occurs when para-sulphamine benzoic acid is heated.
2. When the acid is heated to 285°, the mass becomes completely soluble in water and almost the whole product is acid ammonium parasulphobenzoate, formed at the expense of the charring of part of the mass.

3. When the acid is heated to 220°-235°, infusible parasulphobenzoic diamide is formed, in amounts decreasing with rise in temperature.

4. Two diamides of parasulphobenzoic acid have been isolated, analyzed, and their saponification-products studied. The fusible compound has been shown to contain a carbamine and a sulphamine grouping; to be the amide of parasulphaminebenzoic acid, and thus to be the ordinary diamide. The infusible substance has been shown to differ from the fusible most markedly in its saponification with alkali, and the similarity of its two nitrogen atoms in the molecule has been pointed out.

5. Four products have been isolated from the heating at 220°-235°, including the infusible diamide. Three of these are soluble in water and were identified as acid ammonium parasulphobenzoate, free parasulphobenzoic acid and

a new acid.

6. This latter was saponified with acid and alkali, and proved to act like parasulphaminebenzoic acid, being therefore an isomodification whose constitution is as yet unknown. Barium iso-parasulphaminebenzoate was analyzed and studied. The new acid does not form an ordinary amide by ordinary methods.

7. When parasulphobenzoic and parasulphamine-benzoic acids are heated together, no diamide is formed. Upon this and other facts, the relation between the formation of the diamide, the acid salt and the free acid were brought out, and probable percentages tabulated.

8. When parasulphaminebenzoic acid is transformed to infusible parasulphobenzoic diamide, there is very probably some shifting of nitrogen from union with sulphur to union with carbon.

9. It has been shown that by the action of phosphorpentoxide on parasulphaminebenzoic acid no infusible diamide is formed, a fact which agrees with the theory put forward for the cause of the formation of the latter.

10. The intermediate product of the transformation from parasulphaminebenzoic acid to paracyanbenzenesulphone chloride has been isolated and analyzed. The products formed when this substance, which is shown to be a phosphochloride of parasulphaminebenzoic chloride, is heated, have been identified and the constitution of this compound established.

11. The relation of the phosphochloride to parasulphaminebenzoic acid, on the one hand, and to paracyanbenzenesulphone chloride and parachlorbenzoic nitril on the other, has been definitely developed, thus explaining the action of phosphorus pentachloride in a new light.

Biographical Sketch

Anthony Moultrie Muckenfuss, son of Dr. B. A. Muckenfuss, of Charleston, S.C., was born on Sullivan's Island, S.C., August 5, 1869. He received his primary education in the schools of that city and one of its suburbs, and spent four years at Wofford College, S.C., graduating there in 1889. After two years spent as principal of a high school in his native state, during which time he received the A.M. degree from the above institution, he entered the Johns Hopkins University in the fall of 1891, remaining two years as a graduate student of chemistry and mineralogy. In 1893-4, he taught chemistry and physics at Millsaps College, Jackson, Miss., and during the past year has been on leave of absence continuing his studies here. He has spent a short time under the instruction of Prof. J. W. Mallet, at the University of Virginia.

Subjects: Chemistry, Mineralogy, and Geology.